(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 789 410 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
13.08.1997 Bulletin 1997/33

(51) Int Cl.[6]: **H01M 4/50**, C01G 45/02

(21) Application number: **97300663.8**

(22) Date of filing: **31.01.1997**

(84) Designated Contracting States:
DE FR GB

(30) Priority: **02.02.1996 JP 17279/96**
02.02.1996 JP 17280/96
05.03.1996 JP 47177/96

(71) Applicant: **MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.**
Kadoma-shi, Osaka-fu, 571 (JP)

(72) Inventors:
- **Nunome, Jun**
  Moriguchi-shi, Osaka, 570 (JP)
- **Nakashima, Takuya**
  Neyagawa-shi, Osaka 572 (JP)
- **Yoshizawa, Hiroshi**
  Hirakata-shi, Osaka 573-01 (JP)
- **Toa, Seiji**
  Neyagawa-shi, Osaka, 572 (JP)

(74) Representative: **Crawford, Andrew Birkby et al**
A.A. THORNTON & CO.
Northumberland House
303-306 High Holborn
London WC1V 7LE (GB)

(54) **Batteries and a manufacturing method of postitive active material for the batteries**

(57) This is to improve the heavy-load discharge characteristics of primary battery or to improve the high-rate discharge characteristics of secondary battery by employing manganese oxide on which a surface modified layer is formed as the positive active material wherein said surface modified layer consists mainly of an oxide of at least one element selected out of a group of titanium, cobalt, nickel, strontium, lanthanum and its compound added mainly with a compound made mainly of manganese oxide on the surface of manganese oxide powder consisting of manganese dioxide or a complex oxide of manganese and lithium by using a solution of salt of at least one element selected out of a group of titanium, cobalt, nickel, strontium, and lanthanum to which a manganese salt and a solution to which a solution of manganese salt are added.

EP 0 789 410 A1

Description

BACKGROUND OF THE INVENTION

[Field of the Invention]

The objects of this invention are to offer alkaline-manganese batteries or lithium-ion secondary batteries using the powder of manganese oxides consisting of manganese dioxide or double oxide of manganese and lithium on which a surface modification layer is formed as a positive active material, and a manufacturing method of said positive active materiel for the batteries made-of manganese oxide powder on which a surface modification layer is formed.

[Description of the Prior Arts]

Various primary batteries employing manganese dioxide as the positive active material such as the carbon-zinc dry batteries called Leclanche type or zinc chloride type batteries employing neutral salts of ammonium chloride or zinc chloride as electrolyte, alkaline manganese batteries employing potassium hydroxide as the electrolyte, and Li/MnO_2 system primary batteries belonging to organic electrolyte lithium batteries employing manganese dioxide as the positive active material have been known well.

On the other hand, lithium-ion secondary batteries which can be high-energy density small size rechargeable batteries in next generation have been known also. These batteries employ positive and negative electrodes made of a host material repeating intercalation and deintercalation of lithium-ions by charging and discharging realizing the heavy load discharge, rapid charge, long cyclic life, etc.

Presently, as the host material, a double oxide consisting of cobalt and lithium, or $LiCoO_2$, is used as the positive electrode, while carbon is generally used as the negative electrode. However, because of the unstable world supply comes from the high cost and omnipresence of positive electrode material or cobalt, this is now to be substituted by $LiMnO_2$ or $LiMn_2O_4$ which is a double oxide of manganese and lithium.

As the result of recent power consumption decrease realized by the significant advancement of semiconductor electronics technology, a number of portable electric and electronic apparatuses have been developed and practically used. Various AV apparatuses including the strobe-flash light for still-camera, portable shaver, headphone stereo-player, and LCD-TV are typical of these advancements wherein the demand and the use of alkaline manganese batteries having excellent continuous discharge characteristics are now expanding very rapidly.

However, in contrast to these tendencies, increases of power consumption by the multi-functioned portable apparatuses have been obvious. For example, in the cases of PDA such as portable telephone and facsimile, note-type personal computer and cam-coder, better battery performances taking heavy and continuous loads have been demanded.

Therefore, new built-in type secondary batteries such as the high-capacity nickel-cadmium system, nickel-metal hydride system, or lithium ion type batteries have been developed. And, at the same time, the demands for alkaline manganese batteries capable of continuous discharge at heavy load working as supplementary power source are increasing.

When batteries are continuously discharged, decreases of operating voltages due to the polarization are generally inevitable in proportion to the increase of load current. Thus, the end voltage is reached before the active materials of positive and negative electrode are fully reacted so that the ultimate efficiency of active material remains low.

The polarization lowering of the operation voltage of discharging cell could be attributed for three reasons including the resistance polarization due to the electrical ohmic resistance produced in the outer and inner cell, the activation polarization due -to the charge transfer reaction, and the concentration polarization due to the diffusion control process of reaction substance or products.

Conventionally, in order to improve the continuous heavy load discharge characteristics of alkaline manganese batteries, the amount of electrolytic manganese dioxide (herein-after, abbreviated as EMD) contained in the positive active material has been increased, a high conductivity graphite is used as the conductive material in the positive electrode mix lowering the amount of additives, or a thin separator in which very fine fibers are uniformly distributed has been employed.

Other than these, improvements introducing a gelling agent or a zinc corrosion inhibitor in the negative electrode have been considered effective. Beside this, the employment of a positive electrode of larger polarization in compared to the zinc in the negative electrode has been considered also.

For example, as shown in U.S. Patents 5,277,890 and 5,391,365, methods using EMD powder expanding its specific surface by forming filament-like protrusions thereon by using a chemical synthetic method precipitating MnO2 thereon had been developed. Beside this, a method using a positive electrode to which powder of anatase titanium dioxide is added and mixed as shown in U.S. Patent 5,342,712 had been disclosed.

Although these inventions had been slightly effective increasing the battery service-life at continuous discharge decreasing the polarization comparing over a case where a conventional positive electrode made of EMD powder only is used, these had been effective very little when a heavier load has to be discharged continuously.

The objects of this invention are to offer alkaline-manganese batteries or lithium-ion secondary batteries having longer service lives at heavier load and continuous discharge, and these are made of powder of manganese oxides employing manganese dioxide or double oxide of manganese and lithium on which surface modification layers acting as the positive active material are formed, and a manufacturing method of the positive active materiel for these batteries.

SUMMARY OF THE INVENTION

Though some of the typical improvements of heavy load continuous discharge characteristics of conventional alkaline-manganese batteries have been described so far, most of these are related to the positive electrode of relatively large polarization. The present invention has been proposed from a similar point of view.

Mainly, MnO_2 powder or highly active EMD powder is used as the positive active material of alkaline manganese batteries in most of the cases. Since the electronic conductivity of EMD powder is not necessarily be very high, a conductive agent consisted mainly of graphite having no direct contribution to its conductivity had to be added up to an amount of 10 wt%.

The main discharge reaction of MnO_2 acting as the positive active material in the alkaline electrolyte can be expressed by a uniform solid-phase reaction shown in Eq. (1), wherein not only the improvement of conductivity of active material but the employment of the material minimizing the concentration polarization due to the ion diffusion within the solid phase are desirable.

$$MnO_2 + H_2O + e^- \rightarrow MnOOH + OH^- \qquad (1)$$

The positive electrode potential is expressed by Eq. (2).

$$E = Eo - \frac{RT}{F} \ln \frac{[Mn^{3+}]\,solid}{[Mn^{4+}]\,solid} - \frac{RT}{F} \ln [OH^-] \qquad (2)$$

As shown in above, the present invention is to offer batteries having excellent continuous discharge characteristics realized before even when a heavy load is applied, by employing manganese oxide consisting of EMD powder of which surface is suitably modified as the positive active material having a very little ohmic loss due to the electric resistance and having a small concentration polarization particularly.

More concretely, the objects of the invention are accomplished by batteries employing a positive active material consisting of manganese oxide powder having a surface modified by depositing a layer of compound consisting mainly of oxide of at least one element selected out of a group of titanium (Ti), cobalt (Co), nickel (Ni), strontium (Sr), and lanthanum (La) thereon.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a flow-chart of manufacturing process of the invented positive active material consisting of manganese oxide having a surface modified layer.

Fig. 2 shows examples of comparative transition curves of single electrode potentials of positive active materials made of surface modified by present invention and conventional untreated EMD powder placed in an alkaline electrolyte.

Fig. 3 shows a relationship between the amount of titanium contained in the invented EMD powder of which surface is modified, the electric conductivity, and the gravimetric capacity density thereof.

Fig. 4 shows a half vertical cross-section of LR6(AA) size alkaline manganese battery which is a typical example of the invented battery.

Fig. 5 are drawings comparing the discharge characteristics of alkaline manganese batteries employing invented positive active material having a surface layer modified by nickel compound with the one obtained by employing conventional positive active material made of untreated EMD powder.

Fig. 6 shows a relationship between the total amount of Co and/or Ni contained in the modified surface layer of EMD powder and the discharge capacity ratio.

Fig. 7 shows a discharge characteristics of alkaline manganese battery employing invented positive active material having a surface layer modified by La compound, compared with the one obtained by employing a positive active

material using conventional untreated EMD powder.

Fig. 8 shows a relationship between the total amount of Sr and/or La contained in the surface modified layer of EMD powder and the possible number of pulse discharges.

Fig. 9 shows a cross-sectional view of coin type lithium ion secondary cell which is an other typical example of the invented battery.

Fig. 10 shows a cross-sectional view of R20(D) size zinc chloride type carbon-zinc dry cell which is an other typical example of the invented battery.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A typical structure of the invented alkaline manganese battery and a manufacturing method of the positive active material for the same are now explained here by referring the attached drawings and tables.

<Embodiment-1>

The EMD block electrodeposited on a Ti anode held in a high-temperature manganese sulphate bath kept at a temperature of more than 90°C is peeled off first from the Ti anode. After coarsely crashing and washing the blocks of EMD, this is pulverized by a roller-mill obtaining EMD powder having an average grain diameter of 50 µm, and this is dried by a conventional method before obtaining EMD powder.

After this, The surface of EMD powder is subjected to a modification treatment according to the flow-chart of manufacturing process shown in Fig. 1.

(1) Mixing ...Weighing 300 grams of the EMD powder, this is mixed in an aqueous solution of 3.0 liters containing titanium sulfate of neutral or H_2SO_4 acidity and is dispersed.
(2) Treatment ... By heating the solution holding said EMD powder in a dispersed condition, Ti compound is deposited and coated on the surface of EMD powder modifying the surface thereof. A treatment temperature of 80°C is used in this case. The treatment can be accelerated by bubbling the oxidizing gas such as air, oxygen, or ozone containing the air or oxygen into the solution, or by adding an oxidizing agent such as sodium perchlorate ($NaClO_3$) or sodium persulfate ($Na_2S_2O_8 .2H_2O$) thereto.
(3) Filtration ...The EMD powder of which surface is modified is filtrated in this process, and this process may be replaced by a decantation of the supernatant solution, and this is shifted into the succeeding washing process.
(4) Washing ...Pouring and stirring of pure water, and removal of the supernatant solution is repeated for several times.
(5) Neutralization ...By dropping sodium hydroxide aqueous solution in a state of agitation, the pH thereof is stabilized into a range from 6.0 to 8.0.
(6) Drying...The product is dried for 24 hours at 80°C.

Beside above, the surface modification shown in the processes of (1) - (3), may be replaced by processes of coarse crushing of EMD grain, (4) Washing, (5) Neutralization, and a process of Pulverizing. Furthermore, stabilization and improvements of characteristics of modified EMD are possible by applying a heat treatment in a sulfuric acid aqueous solution after Treatment of (2).

The electric conductivity, moistures, and the discharge capacity ratios of positive active materials determined by changing the addition of sulfuric acid (H_2SO_4) to $Ti(SO_4)_2$ aqueous solution and the type of oxidizing agent are listed in Table 1 shown below.

Table-1

Sample No.	1	2	3	4	5	6	7	8	9	10	11
Composition of Treatment Solution											
$Ti(SO_4)_2$(mol/1)	-	0.2	0.2	0.2	0.2	0.2	0.2	-	0.2	0.2	0.2
H_2SO_4 (mol/1)	-	2.0	2.0	2.0	2.0	2.0	2.0	2.0	-	-	-
Oxidizing Agent											
Air (ml/min)	-	-	-	-	50	-	-	-	-	50	-
O_2 (ml/min)	-	-	-	-	-	50	-	-	-	-	-
O_3 (ml/min)	-	-	-	-	-	-	50	-	-	-	-
Na_2ClO_3	-	O	-	-	-	-	-	-	O	-	-

Table-1 (continued)

Sample No.	1	2	3	4	5	6	7	8	9	10	11
$Na_2S_2O_8 2H_2O$	-	-	O	-	-	-	-	-	-	-	-
Electric Conductivity ($x10^{-3}$S/cm)	13.7	995	990	800	930	950	950	14.0	810	870	570
Moisture(wt%)	4.58	4.90	4.80	4.20	4.55	4.35	4.43	4.12	4.05	4.32	4.55
Discharge Capacity Ratio	100	107	106	105	107	107	106	101	105	106	104

In Table 1, the ozone (O_3) content in the oxidizing agent means direct bubbling of oxygen (O_2). including the O_3 generated by the flow-in of O_2 into the ozonizer at a flow rate of 50 ml/min into the treatment solution.

The electric conductivity is determined by placing the sample powder of predetermined volume in a die made of PTFE, and by measuring the terminal DC resistance at a state where a pressure of 3t/cm^2 is applied. The moisture is determined by reducing the weight of sample heated and dehydrated at 500°C from the weight of sample dried at 105°C.

In addition to these, preparing a working positive electrode by pressing a mixture of sample powder of 10 weight part mixed with acetylene black of 1 weight part on to a platinum (Pt) plate, using a counter electrode made of Pt plate and a reference electrode made of Hg/HgO, and by measuring the capacity of the positive electrode potential reaching to a potential of -300 mV from the reference electrode potential applying a constant current of 10 mA per one gram of the sample in an alkaline electrolyte consisting of 40 wt% potassium hydroxide (KOH) aqueous solution dissolving 3.0 wt% zinc oxide (ZnO), and the capacity ratios of each sample are derived defining the capacity of the EMD powder sample No. 1 as 100.

In here, the discharge end potential of -300 mV is employed as a potential corresponding to the discharge ending voltage of alkaline manganese battery which is 0.9 V.

Table 1 shows that all of the electric conductivity of Samples Nos. 2 - 7 and Nos. 9 - 10 obtained by treating the EMD powder in a $Ti(SO_4)_2$ aqueous solution are higher by about two orders comparing to that of untreated EMD powder Sample No. 1. Among these, tendencies of slightly higher electric conductivity are observed when H_2SO_4 is added to the treatment solution (Sample Nos. 2 - 7). These tendencies are obvious particularly when H_2SO_4 is added together with the oxidizing agent (Sample Nos. 2, 3, 5, 6, and 7). In addition to these, no particular differences depending on the type of oxidizing agent have been observed.

The electron-microscopic observations made on the surfaces of untreated EMD powder of Sample No. 1 and those of Sample No. 2 obtained by treating the EMD powder in a H_2SO_4 acidity $Ti(SO_4)_2$ aqueous solution being added by an Na_2ClO_3 oxidizing agent, proved a little surface irregularity of Sample No. 1 while less irregularities on Sample No. 2 which could attributed for the irregularities smoothed out by the deposition.

Since a moisture up to 5 wt.% is contained in EMD powder usually, the content of MnO_2 and the electric conductivity could be increased by the removal of moisture which could be done by applying a heat treatment. However, sacrificing the capacity on the other hand by the positive electrode potential lowered by the discharge in the alkaline electrolyte.

Table 1 proves that not only the electric conductivity improved by two orders but the significantly increased discharge capacity can be obtained without reducing the moisture by using the EMD powder on which a surface modified layer is formed by using a Ti compound,

It has been confirmed that the content of titanium in Sample No. 2 is close to 1.8 wt.% by using an element analysis method. Thus, this is attributed for the EMD powder of which entire or partial surface is modified by the thin deposition of titanium compound consisting mainly of titanium oxide. Although the exact determination of the thickness of surface modified layer is found impossible because of its extremely thin thickness even with an X-ray diffraction method. However, the effectiveness of the surface modified layer is obvious.

Fig. 2 shows two discharge characteristics of unipolar electrode potential in an alkaline electrolyte obtained with Sample Nos. 1 and 2.

In Fig. 2, while a rapid potential decrease of Sample No. 1 employing untreated EMD powder at the ending of discharge is observed, a gentle potential decrease of Sample No. 2 employing the EMD powder on which a surface layer modified by a titanium compound is found, and this could be attributed for the significant capacity improvement thereof. In addition to this, no particular effect of surface modification has been observed with Sample No. 8 employing the EMD powder treated by sulfuric acid, and very little change with Sample No. 1 is observed.

<Embodiment-2>

Fixing the concentration of sulfuric acid in the treatment solution at 2.0 mol/l, various surface modified EMD powders of different titanium contents are prepared in accordance to Embodiment-1 changing the concentration of $Ti(SO_4)_2$ and

the treatment condition.

From these, the gravimetric capacity densities (mAh/g) are determined from the measurements of electric conductivity and the single electrode discharge tests, and the results of these are shown in Fig. 3.

Fig. 3 shows also a steady increase of the electric conductivity in proportion to the increase of Ti content in contrast to that of Sample No. 1 which is fixed at 13.7 x 10^{-3} S/cm, and shows also a near saturation of electric conductivity at a point exceeding 0.1 wt.%. On the other hand, the gravimetric capacity density is found optimum in a range of titanium content from 0.1 - 5.0 wt.%.

<Embodiment-3>

Various positive active materials of which surfaces are modified are prepared by adding salts of manganese, nickel, or cobalt to the H_2SO_4 acidity $Ti(SO_4)_2$ treatment solution according to the case of Embodiment-1, and the electric conductivity, moistures, and the apparent densities thereof are measured. Then, preparing various LR6(AA) type alkaline manganese batteries, the discharge capacity ratios at heavy and medium loads are determined.

A cross-section of experimental LR6 size alkaline manganese battery is shown in Fig. 4 wherein the cap 1A made of nickel plated steel acting its positive terminal is integrally molded-, and conductive coating 1B made of carbon paint is coated on the inner wall of the positive can 1.

Then, manganese oxide made either of untreated EMD powder or various surface modified EMD powder mixed with graphite at a weight ratio of 9 to 1 is press-molded into a shape of cylinder, and four of the cylinders are inserted into said positive can 1, and positive electrode mold 2 is press- molded on the inner wall of positive can 1.

Inserting cylinder-shaped separator 3 and bottom plate 3A within positive electrode mold 2, gel negative electrode 4 prepared by dispersing the zinc powder of 2 weight part in a viscose solution of 1 weight part dissolving a gelling agent made of carboxymethyl cellulose (CMC) or polysodium acrylate or others into said alkaline electrolyte is injected.

Then, negative electrode terminal 6 made of nickel-plated steel on which brass current collector 5 is welded and washer 7 are integrated by plastic sealer 8, and this unit is inserted into gel negative electrode 4. At a condition where sealer 8 is placed on groove 1C formed by inwardly curling the opening of positive can 1, the upper edge of said can 1 is curled inwardly sealing the can. This cell assembly process is ended by sticking label 9 thereon at the end.

The discharge test of each cell is performed under a heavy load giving a constant current of 1000 mA and under a medium load giving a constant resistance of 10 ohms continuous discharge, obtaining a discharge-end voltage of 0.9 V in both cases. Table 1 shows a tabulation of discharge periods where the discharge period obtained by Sample No. 1 cell employing a positive active material made of untreated EMD powder is defined as 100, and the ones of other cells each employing positive active material made of treated EMD powder of which surface layer is modified are defined as the ratios of those to that of Sample No. 1.

The results of these are tabulated in Table 2.

Table 2

Sample No.	1	2	12	13	14	15	16	17	18	19	20
Composition of Treatment Solution											
$Ti(SO_4)_2$(mol/l)	-	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
H2SO_4(mol/l	-	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
$MnSO_4$(mol/l)	-	-	0.2	-	-	0.2	0.2	-	0.2	0.2	0.2
$CoSO_4$(mol/l)	-	-	-	0.2	-	0.2	-	0.2	0.2	0.2	0.2
$NiSO_4$(mol/l)	-	-	-	-	0.2	-	0.2	0.2	0.2	0.2	0.2
Kind of Oxidizing Agent											
Air (ml/min)	-	-	-	-	-	-	-	-	-	50	-
O_2 (ml/min)	-	-	-	-	-	-	-	-	-	-	50
Na_2ClO_3	-	o	o	o	o	o	o	o	o	-	-
Electric Conductivity (x10^{-3}S/cm)	13.7	995	990	990	930	950	950	950	970	980	920
Moisture(wt.%)	4.58	4.9	4.2	4.2	4.55	4.15	4.13	4.12	4.05	4.12	4.15
Apparent Density(g/cm^3)	2.67	2.60	2.92	2.65	2.66	2.93	2.90	2.64	2.96	2.87	2.89

Table 2 (continued)

Sample No.	1	2	12	13	14	15	16	17	18	19	20
Heavy load Discgarge Capacity Ratio	100	100	100	105	105	103	103	105	105	105	105
Medium Load Discharge Capacity Ratio	100	107	106	105	105	107	106	102	105	106	104

While the electric conductivity of untreated EMD powder of Sample No. 1 is 13.7 x 10^{-3}S/cm, those of the others using the treatment which includes titanium salt solution containing either the salt of manganese, nickel, cobalt, etc., are higher by two orders. Moistures of Sample Nos. 12, 15, 16, 18, 19 and 20 added with manganese salt are found slightly less than that of Sample No. 1, and a slight increase of the apparent densities is found also.

These could be attributed for a possible deposition of chemical manganese dioxide (CMD) having a fundamentally low moisture (less than 1.0%) on EMD simultaneously with the deposition of a compound consisting mainly of titanium oxide.

Considerably improved heavy load discharge characteristics are found with Sample Nos. 13 - 20 depositing a cobalt and/or nickel compound mixed with a titanium compound.
Said considerable improvements of heavy load discharge characteristics can not be explained only by the nobler potential of CoOOH and/or NiOOH of cobalt and/or nickel oxide deposited together with the titanium oxide, but it could be probably explained by the suppressed concentration polarization together with the suppressed resistance polarization took place during the discharge.

Moreover, since the electric conductivity of surface modified EMD including the titanium compound is improved, the content of conductive agent such as graphite could be reduced at a level less than 10 wt.%. However, the dependency on the type of oxidizing agents has not been clarified.

<Embodiment-4>

In Embodiment-3 described before, the improvements of heavy load discharge characteristics of alkaline manganese batteries by employing the EMD powder of which surface is modified by a titanium compound together with a compound of cobalt and/or nickel compound and the cobalt and/or nickel compound including the manganese compound has been explained.

Therefore, in Embodiment-4 shown here, LR6 size alkaline manganese batteries utilizing a positive active material formed on the EMD powder of which surface layer is modified are prepared in accordance to Embodiemnt-1 using a solution of cobalt salt and/or nickel salt, or cobalt salt and/or nickel salt including the manganese salt excluding the use of titanium salt in the treatment solution.

All of these batteries are subjected to a continuous discharge test supplying a constant current of 1500 mA (obtaining an end voltage of 0.9 V), and the discharge capacity ratios of those batteries defining that obtained by Sample No.1 using untreated EMD powder as 100 are determined. The results of those are shown in Tables 3, 4, and 5.

Table 3

Sample No.	1	21	22	23	24	25	26	27	28	29
Composition of Treatment Solution										
H_2SO_4 (mol/1)	-	2.0	2.0	2.0	2.0	2.0	2.0	-	-	-
$CoSo_4$ (mol/l)	-	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Oxidizing Agent										
Air (ml/min)	-	-	-	-	50	-	-	-	-	50
O_2 (ml/min)	-	-	-	-	-	50	-	-	-	-
O3 (ml/min)	-	-	-	-	-	-	50	-	-	-
Na_2ClO_3	-	-	o	-	-	-	-	-	o	-
$Na_2S_2O_8.2H_2O$	-	-	-	o	-	-	-	-	-	-
Discharge Capacity Ratio	100	104	106	106	105	104	106	104	104	106

Table 4

Sample No.	1	30	31	32	33	34	35	36	37	38
Composition of Treatment solution										
H_2SO_4(mol/l	-	2.0	2.0	2.0	2.0	2.0	2.0	-	-	-
$NiSO_4$(mol/l)	-	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Kind of Oxidizing Agent										
Air (ml/min)	-	-	-	-	50	-	-	-	-	50
O_2 (ml/min)	-	-	-	-	-	50	-	-	-	-
O_3 (ml/min)	-	-	-	-	-	-	50	-	-	-
Na_2ClO_3	-	-	o	-	-	-	-	-	o	-
$Na_2S_2O_8.2H_2O$	-	-	-	o	-	-	-	-	-	-
Discharge Capacity Ratio	100	105	107	106	107	107	106	104	105	106

Table 5

Sample No.	1	39	40	41	42	43	44	45	46	47	48
Composition of Treatment Solution											
H_2SO_4 (mol/1)	-	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	-	-
$CaSO_4$ (mol/l)	-	0.2	-	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
$NiSO_4$ (mol/1)	-	0.2	0.2	-	0.2	0.2	0.2	0.2	0.2	0.2	0.2
MnSO4 (mol/1)	-	-	0.2	0.2	0.2	0.2	0.2	0.2	0.2	-	0.2
Oxidizing Agent											
Air (ml/min)	-	-	-	-	-	-	50	-	-	-	-
O_2 (ml/min)	-	-	-	-	-	-	-	50	-	-	-
O_3 (ml/min)	-	-	-	-	-	-	-	-	50	-	-
Na_2ClO_3	-	o	o	o	o	-	-	-	-	-	-
$Na_2S_2O_8.2H_2O$	-	-	-	-	-	o	-	-	-	-	-
Apparent density(g/cm^3)	2.67	2.65	3.03	2.98	2.92	2.92	2.97	3.00	3.01	2.66	2.88
Discharge Capacity Ratio	100	106	105	105	106	107	106	107	105	104	105

Respective examples of 1500 mA constant current continuous discharge characteristics of alkaline manganese battery using the positive active material employed by Sample No. 1 and Sample No. 30 are shown in Fig. 5.

Fig. 5 shows a higher discharge capacity up to a discharge end voltage of 0.9 V since the discharge voltage is improved by using EMD powder of which surface layer is modified by a nickel compound made- mainly of nickel oxide which could be NiOOH used as the positive electrode.

Beside this, no noticeable difference between the points at which the discharge capacity is lost and the discharge voltage is rapidly decreased have been observed.

In the cases where the surface of EMD powder is modified by introducing a Co and/or Ni compound or a Co and/or Ni compound containing a Mn compound into the treatment solution, tendencies realizing a slightly higher discharge voltage and discharge capacity ratio have been observed when the treatment solution of H_2SO_4 acidity (Samples Nos. 21 - 26, 30 - 35, and 39 - 46) is used compared with the case where the treatment solution of no H_2SO_4 acidity is used.

Moreover, though no particular effect of the oxidizing agent type have been observed in this case, slightly improved discharge characteristics realized by the introduction of an any oxidizing agent in the treatment process have been seen.

In this embodiment also, like the case of Embodiment-3, the higher apparent density realized by the introduction of manganese salt in the treatment solution have been observed.

Fig. 6 shows a relationship between the discharge capacity ratio of positive electrode made of EMD powder of which surface is modified by the deposition of Co and/or Ni compound and the total contents of Co and/or Ni. Like the cases of Embodiments-1 and -2, the discharge capacity ratios are determined by conducting single electrode discharge

tests in an alkaline electrolyte and defining the one obtained by the untreated END powder as 100. Fig. 6 shows also the discharge capacity ratios of every EMD powder of which surface layers are modified by using a Co and/or Ni compound, and these are higher than that (240 mAh/g) of untreated EMD powder. Note is the effectiveness of total contents of Co and/or Ni in a range from 0.1 - 10.0 wt%. in these cases.

Electron-microscopic observations made on the surface of EMD powder modified by a Co and/or Ni compound and a Co and/or Ni compound containing a Mn compound, like the case where the surface is modified by a Ti compound, has proved the order of surface irregularities less than those observed on the untreated EMD powder. Moreover, like the cases of Embodiments -3 and -4, the higher apparent densities of surface modified EMD powder containing a Mn compound (Sample Nos. 40 - 46 and 48) are observed.

<Embodiment-5>

The Embodiments -1 - -4 have proved the effectiveness of EMD powder of which surfaces are modified by forming a Ti compound or a Co (cobalt) and/or Ni (nickel) compound and by forming a Ti compound containing Mn or Co and/ or Ni compound. In this Embodiment-5, the effects of the surface modification by using a Sr (strontium) and/or La (lanthanum) compound, and by using a Sr (strontium) and/or La (lanthanum) compound containing Mn compound are confirmed.

Like the case of Embodiment-1, various LR6-size alkali manganese batteries employing the EMD powder of which surface is modified by a Sr (strontium) and/or La (lanthanum) compound, and by a Sr (strontium) and/or La (lanthanum) compound containing a Mn compound as its positive active material are prepared, and these are subjected to a pulse discharge test.

The pulse discharge test is a test simulating a strobe flash for still-camera where the discharge is repeated for a 15 sec., on a constant resistance of 1.8 ohm allowing a rest period of 45 sec., are the number of the discharges is counted until an end voltage of 0.9 V is reached. Defining the number of pulse discharges obtained by the cell of Sample No. 1 employing untreated EMD powder is 100, the ratio of the number of pulse discharges obtained by a cell employing surface modified EMD powder is expressed by the discharge capacity ratio. These results are shown in Tables 6, 7, and 8.

Some examples of the 1500 mA constant current discharge characteristics of LR6-size alkaline manganese batteries prepared by employing untreated EMD powder, and the ones employing the positive active material employing the EMD powder (Sample No. 58) of which surface is modified by a La compound are shown in Fig. 7.

Table 6

Sample No.	1	49	50	51	52	53	54	55	56	57
Composition of Treatment solution										
H_2SO_4(mol/l	-	2.0	2.0	2.0	2.0	2.0	2.0	-	-	-
$SrSO_4$(mol/l)	-	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Kind of Oxidizing Agent										
Air (ml/min)	-	-	-	-	50	-	-	-	50	-
O_2 (ml/min)	-	-	-	-	-	50	-	-	-	-
O_3 (ml/min)	-	-	-	-	-	-	50	-	-	-
Na2ClO3	-	o	-	-	-	-	-	o	-	-
$Na_2S_2O_8.2H_2O$	-	-	o	-	-	-	-	-	-	-
Discharge Capacity Ratio	100	106	106	104	105	104	104	105	106	103

Table 7

Sample No.	1	58	59	60	61	62	63	64	65	66
Composition of Treatment Solution										
H_2SO_4 (mol/1)	-	2.0	2.0	2.0	2.0	2.0	2.0	-	-	-
$LaSO_4$ (mol/l)	-	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Oxidizing Agent										
Air (ml/min)	-	-	-	-	50	-	-	-	50	-
O_2 (ml/min)	-	-	-	-	-	50	-	-	-	-

Table 7 (continued)

Sample No.	1	58	59	60	61	62	63	64	65	66
O_3 (ml/min)	-	-	-	-	-	-	50	-	-	-
Na_2ClO_3	-	o	-	-	-	-	-	o	-	-
$Na_2S_2O_8.2H_2O$	-	-	o	-	-	-	-	-	-	-
Discharge Capacity Ratio	100	107	106	105	107	107	106	105	106	104

Tables 6, 7 and 8 show that all of the discharge capacity ratio obtained with EMD powders on which surface modified layers are formed by a Sr and/or La compound and a Sr and/or La compound containing Mn compound are higher than that obtained with untreated EMD powder (Sample No.1), as improved discharge voltage.

In addition to these, a slight improvement of discharge capacity ratio is seen when the treatment solution is acidified by H_2SO_4 and when an oxidizing agent of any type is employed although no obvious dependency on the type of oxidizing agent is seen in this case also.

Like the cases of Embodiments -3 and -4, higher apparent densities are observed with the EMD powders of which surfaces are modified by mixing a Mn compound in the layer. Moreover, apparent from Fig. 7, since the heavy load discharge voltage of the cell (Sample No. 58) employing the EMD powder of which surface is modified by La compound is higher than that employing the untreated EMD powder (Sample No. 1), an increase of discharge capacity up to a voltage of 0.9 V is seen. However, no particular difference in the total capacity is observed.

Table 8

Sample No	1	67	68	69	70	71	72	73	74	75	76
Composition of Treatment solution											
H_2SO_4(mol/l)	-	2.0	2.0	2.0	2.0	2.0	2.0	2.0	-	-	-
$SrSO_4$(mol/l)	-	0.2	-	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
$LaSO_4$(mol/l)	-	0.2	0.2	-	0.2	0.2	0.2	0.2	0.2	0.2	0.2
$MnSO_4$(mol/l)	-	-	0.2	0.2	0.2	0.2	0.2	0.2	0.2	-	0.2
Kind of Oxidizing Agent											
Air (ml/min)	-	-	-	-	-	-	50	-	-	-	-
O_2 (ml/min)	-	-	-	-	-	-	-	50	-	-	-
O_3 (ml/min)	-	-	-	-	-	-	-	-	50	-	-
Na_2ClO_3	-	o	o	o	o	-	-	-	-	-	-
$Na_2S_2O_8.2H_2O$	-	-	-	-	-	o	-	-	-	-	-
Apparent Density (g/cm^{-3})	2.67	2.63	3.01	2.97	2.92	2.92	2.95	3.0	3.01	2.64	2.84
Discharge Capacity Ratio	100	105	105	105	106	107	106	107	105	103	103

All of the cells employing the other EMD powder of which surface is modified by another Sr and/or La compound and by a Sr and/or La compound including the Mn compound showed similar behaviors.

Fig. 8 shows a relationship between the pulse discharge cycle counts of LR6-size alkaline manganese batteries employing the EMD powder of which surface is modified by depositing a Sr and La compound as its positive active material and the total contents of Sr and La. Fig. 8 shows also that all of the batteries employing EMD powder of which surface is modified by a Sr and/or La compound show definite improvements of pulse discharge cycle counts, and it is particularly effective when the total content of Sr and/or La is in a range from 0.1 - 10.0 wt%.

In addition to this, an electron microscopic observation made on the EMD powder of which surface modified by a Sr and/or La compound and a Sr and/or La compound containing Mn compound have proved less surface irregularities like the other EMD powder of which surface is modified. In addition to this, higher apparent densities with the surface modified EMD powders containing Mn compound (Sample Nos. 68 -74 and 76) is obtained like the other cases.

<Embodiment-6>

The performance of the positive active material developed for non-aqueous electrolyte secondary batteries of

Sample Nos. 1 - 76 shown in Embodiments -1 - -5 have been tested.

A cross-section of coin type cell developed for the evaluation of invented positive electrode is shown in Fig. 9 wherein 21 is a cell-case made of stainless-steel anti-corrosive to the organic electrolyte, 22 is a cell cover made of the same material, 23 is an invented positive electrode, 24 is a current collector for positive electrode 23 made of the same stainless-steel and is spot-welded to the internal surface of cell-case 21, 25 is negative electrode molded graphite powder and pressed against the inside of cell cover 22. 26 is a separator made of porous polypropylene, and 27 is an insulating gasket made of polypropylene. The evaluation cell coin type has a diameter of 20 mm and an overall height of 1.5 mm.

The positive active material is prepared by mixing various surface modified EMDs prepared in advance with lithium hydroxide (LiOH) at a ratio forming a double oxide of manganese and lithium, $LiMn_2O_4$ of prescribed composition, and this mixture is sintered at a temperature of 860°C for 70 hours in an oxidizing atmosphere. The positive electrode compound is prepared by mixing a conductive agent into polyvinylidenfluoride acting as a binder at a weight part of 5 to 5, and by mixing this mixture into the obtained positive active material at a weight part of 90. Preparing the electrode by molding thus obtained positive electrode compound of a -prescribed volume on current collector 24, this is dried at a temperature of 150°C in vacuum condition, and this is assembled into a cell using a negative electrode 25.

As an electrolyte, lithium perchlorate dissolved in a solvent where ethylene carbonate and 1, 3-dimethoxyethane are mixed at an equal volume obtaining a concentration of 1 mol/litter is used. Since positive electrode is deintercalated lithium-ions electrochemically to electrolyte by charging after the cell assembly, and intercalated the lithium ions from electrolyte by discharging, it is obvious that this functions as a positive electrode material for secondary batteries.

These evaluation cells were charged up to a voltage of 4.2 V at a rate of 0.2 mA/cm^2, and then discharged to a voltage of 3.0 V at a rate of 0.2 mA/cm^2 and 1.0 mA/cm^2 at an ordinary temperature, and the discharge characteristics depending on the difference of discharge rate have been determined.

Table 9 shows the ratio of discharge capacity at a rate of 1.0 mA/cm^2 to that at a rate of 0.2 mA/cm^2.

In here, the tests are conducted for Sample Nos. S-2, -9, -13, -14, -22, -31, -50, and -59 employing a concentration of sulfuric acid of 2.0 mol/l and a concentration of various sulfate of 0.2 mol/l as a condition of surface modification treatment, and employing sodium perchlorate as an oxidizing agent, the results of these are compared with that of EMD powder of Sample No. S-1 used as a starting material.

Table 9

Sample No.	S-1	S-2	S-9	S-13	S-14	S-22	S-31	S-50	S-59
Discharge Capacity Ratio(%)	88	93	89	92	92	91	91	90	90

As shown in Table 9, the surface modified samples show better high-rate discharge characteristics than the one obtained by the referenced sample No.S-1. Moreover, the same effects could be obtained if the surface modification were made on the samples mentioned other than the above.

<Embodiment-7>

Using the materials of Sample Nos. 1 - 76 shown in Embodiemnts-1 -5 as a positive active material and zinc as a negative active material, the zinc chloride type carbon-zinc dry cells shown in Fig. 10 are prepared.

In Fig. 10, 31 is a positive electrode mix, 32 is a carbon rod acting as a positive current collector, 33 is a zinc can, 34 is a separator, 34A is a bottom paper, 35 is a plastic sealing cover, 35A is a positive terminal plate, 36 is a cover paper, 36A is sealer, 37 is a negative terminal plate, 38 is a PVC tube, and 39 is a metal jacket. Positive electrode mix 31 is prepared by mixing said manganese dioxide with acetylene-black at a weight ratio of 5 : 1, by mixing this into an electrolyte consisting of zinc chloride and ammonium chloride mixed solution, which main constituent is zinc chloride, and by molding.

R20 (D) size carbon-zinc dry cells are prepared thus, and these are continuously discharged for a load of 2 Ohms at room temperature (20°C), and the end voltage is down to 0.9 V. The results of these are shown in Table 10.

Table 10

Sample No.	1	2	5	12	13	14	24	33	52	61
Discharge Duration Ratio	100	106	105	105	104	105	104	105	104	104

As shown in Table 10, carbon-zinc dry cells show better heavy-load discharge characteristics when a manganese dioxide having a surface modified layer is employed over the cases where the cells employ a manganese dioxide having a unmodified surface layer.

Taking an example for mainly an alkaline manganese battery prepared by employing an EMD powder having a surface modified layer by compound consisting mainly of oxide of at least one element selected out of a group of Ti-, Co, Ni, Sr, and La, and is used as the positive active material, the resistance polarization and the concentration polarization are obviously lowered at the heavy load and continuous discharge so that discharge characteristics of high efficiency can be obtained by the increased discharge voltage and the effective capacity.
Those cases wherein a Mn compound is introduced in the surface modified layer are found effective also.

The effects available with the above-mentioned surface layer modification are not necessarily be limited to the alkali manganese batteries only. By conducting a surface modification depositing a compound of at least one element selected out of a group of Ti, Co, Ni, Sr, and La on the surface of not only EMD but CMD and natural manganese dioxide (NMD), and by using this as a positive active material, those can be applied to Leclanche type and zinc chloride type carbon-zinc dry batteries also.

Moreover, by applying a heated dehydration treatment at a temperature from 350 - 450°C to said surface modified manganese dioxide powder, the positive active material for the Li/MnO_2 system organic electrolyte lithium primary battery having a high rate discharge characteristics can be obtained.

Furthermore, by using a manganese oxide on which a surface modified layer is formed by depositing a compound of at least one element selected out of a group of Ti, Co, Ni, Sr, and La on the surface of $LiMnO_2$ or $LiMn_2O_4$ powder which is a double oxide of Mn and Li repeating the deintercalation and intercalation of Li by charge and discharge as the positive electrode, still-better charge and discharge characteristics can be obtained.

In these embodiments, although an example using a sulfate aqueous solution as the treatment solution for surface modification has been shown, the treatment solution of this invention in not necessarily be limitedwithin the usage of sulfates.

That is, when chlorides or nitrates etc, are used as the positive active material of the battery after the treatment, the use of these salt can never be disturbed by the possible introduction of minute anions contained in the treatment solution. For instance, it could be well understood that the use of chloride solution as the treatment solution acting as the positive active material for carbon-zinc dry batteries wherein NH_4Cl and/or $ZnCl_2$ is used as an electrolyte.

This invention is to offer batteries using a manganese oxide on which the surface of manganese oxide powder consisting of MnO2, Mn and Li of a double oxide is modified by the deposition of a compound consisting mainly of an oxide of at least one element selected out of a group of Ti, Co, Ni, Sr, and La as its positive active material and a compound made mainly of a Mn oxide by using a solution dissolving a salt of at least one element selected out of a group of Ti, Co, Ni, Sr, and La to which a Mn salt is added.

And this is highly effective to improve the heavy load continuous discharge characteristics of primary batteries such as carbon-zinc dry batteries, alkaline manganese batteries, and Li/MnO_2 system organic electrolyte lithium batteries.

Furthermore, further improvements of high-rate charge and discharge characteristics with the lithium-ion secondary batteries can be expected also. These could be possible by the reduction of resistance polarization and/or concentration polarization of the positive active material used therein.

Claims

1. Batteries employing manganese oxides consisting of a manganese dioxide or a double oxide of manganese and lithium on which a surface modification layer is formed by deposition of a compound consisted mainly of oxide of at least one element selected from a group of titanium, cobalt, nickel, strontium, and lanthanum as the positive active material.

2. Batteries according to Claim 1 employing a compound made mainly of manganese oxide dispersed in said surface modification layer.

3. Carbon-zinc dry batteries according to Claims 1 and 2 employing manganese dioxide powder on which a surface modification layer is formed as the positive active material.

4. Alkaline manganese batteries employing manganese dioxide powder on which surface modification layer is formed as the positive active material according to Claims 1 or 2.

5. Alkaline manganese batteries employing electrolytic manganese dioxide powder as the positive active material on which surface modification layer is formed according to Claims 1 and 2.

6. Organic lithium primary batteries employing heated and dehydrated manganese dioxide powder as the positive

active material after forming a surface modification layer according to Claims 1 and 2.

7. Lithium-ion secondary batteries employing powder of a double oxide of manganese and lithium as the positive active material after forming a surface modification layer according to claim 1 or 2.

8. A manufacturing method of positive active material for batteries by which a surface modification layer is formed by depositing a compound consisting mainly of an oxide of at least one element selected out of a group of titanium, cobalt, nickel, strontium, and lanthanum by dispersing a manganese oxide powder consisting of a manganese dioxide or a double oxide of manganese and lithium in a treatment solution of salt of at least one element selected out of a group of titanium, cobalt, nickel, strontium and lanthanum.

9. A manufacturing method of positive active material for batteries according to Claim 8 by which a compound consisting mainly of manganese oxide is dispersed in a surface modification layer by the addition of manganese salt in said treatment solution.

10. A manufacturing method of positive active material for batteries according to Claims 8 and 9 by which a salt of an element selected out of a group of titanium, manganese, cobalt, nickel, strontium, and lanthanum used to said treatment-solution is at least a type of salt selected out of sulfate, nitrate, and chloride.

11. A manufacturing method of positive active material for batteries according to Claims 8, 9, and 10 by which the surface modification is performed keeping the acidity of said treatment solution.

12. A manufacturing method of positive active material for batteries according to Claim 8 to claim 11 by which the surface modification layer is formed by adding at least one oxidizing agent selected out of a group of air, oxygen, ozone, sodium perchlorate, and sodium persulfate.

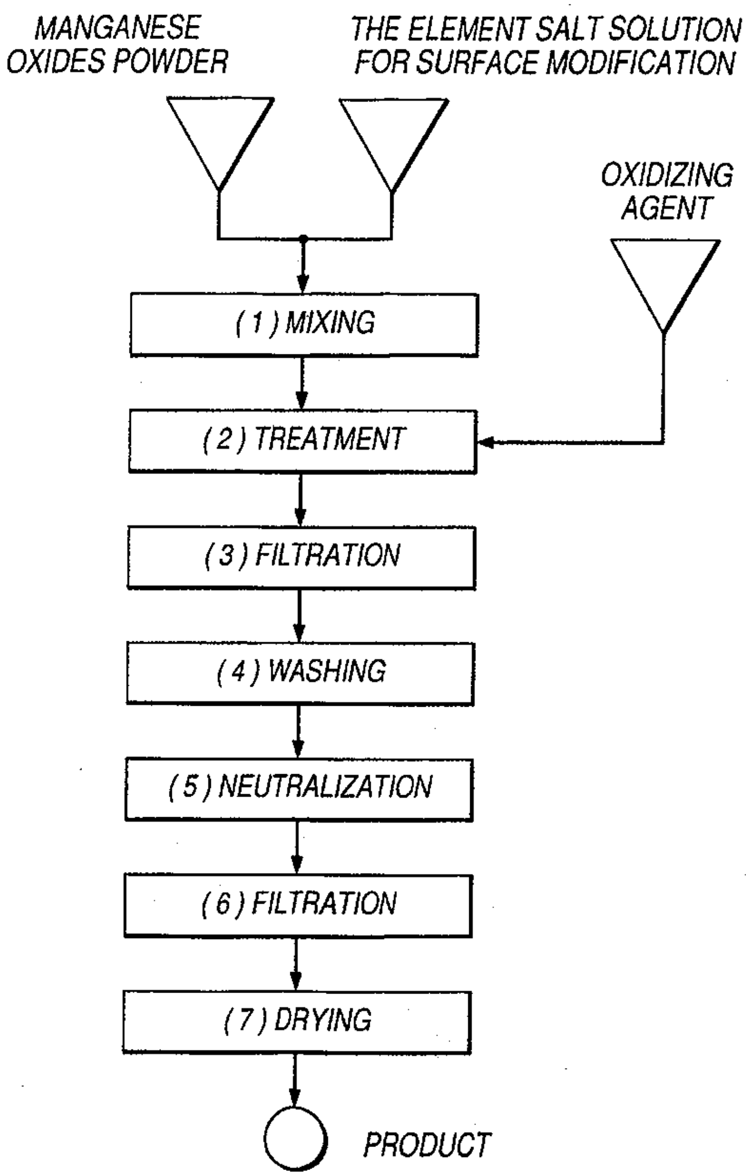
MANGANESE OXIDES POWDER
THE ELEMENT SALT SOLUTION FOR SURFACE MODIFICATION
OXIDIZING AGENT
(1) MIXING
(2) TREATMENT
(3) FILTRATION
(4) WASHING
(5) NEUTRALIZATION
(6) FILTRATION
(7) DRYING
PRODUCT

Fig. 1

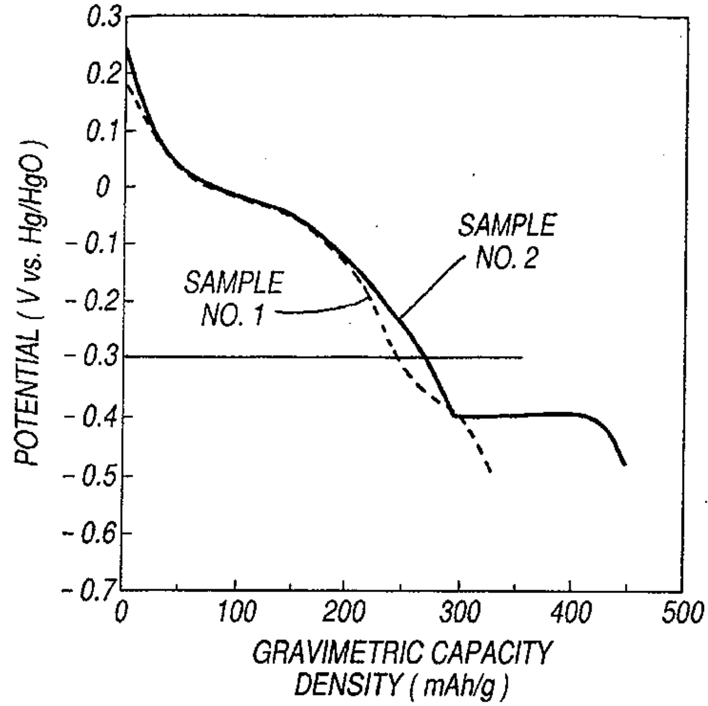
0.3
0.2
0.1
0
- 0.1
- 0.2
- 0.3
- 0.4
- 0.5
- 0.6
- 0.7
POTENTIAL (V vs. Hg/HgO)
SAMPLE NO. 2
SAMPLE NO. 1
0
100
200
300
400
500
GRAVIMETRIC CAPACITY DENSITY (mAh/g)

Fig. 2

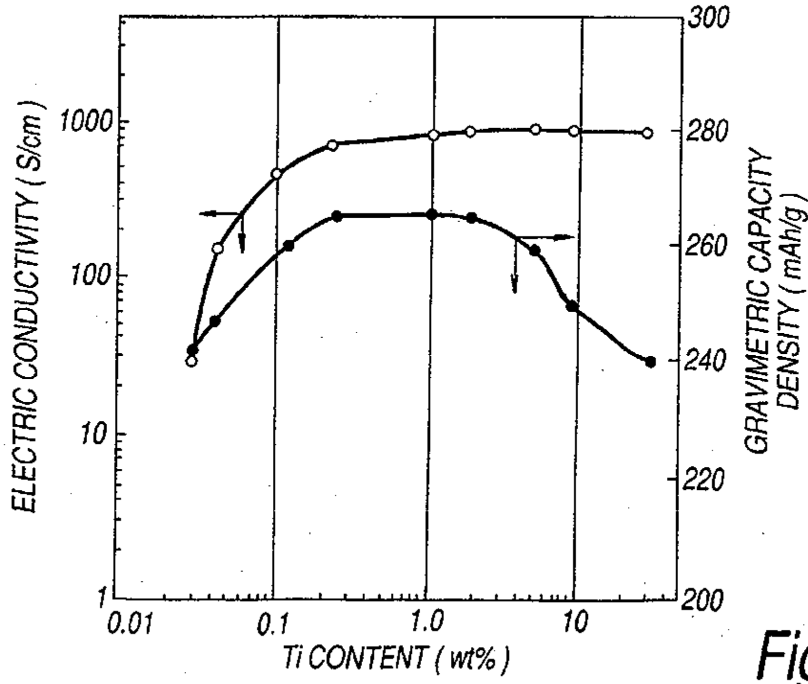
1000
100
10
1
ELECTRIC CONDUCTIVITY (S/cm)
300
280
260
240
220
200
GRAVIMETRIC CAPACITY DENSITY (mAh/g)
0.01
0.1
1.0
10
Ti CONTENT (wt%)

Fig. 3

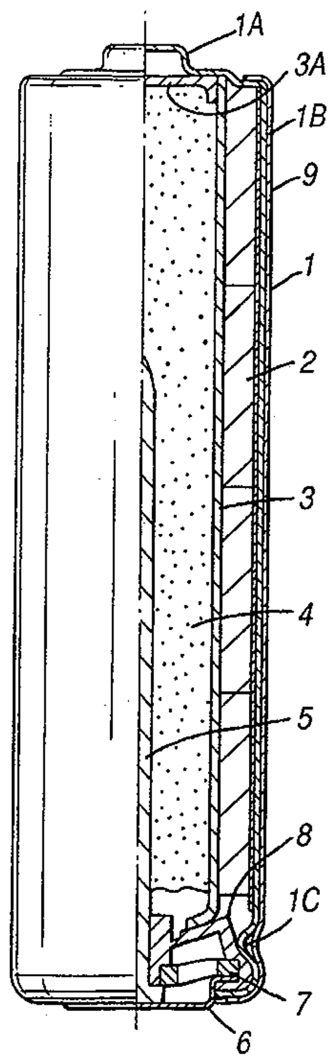

Fig. 4

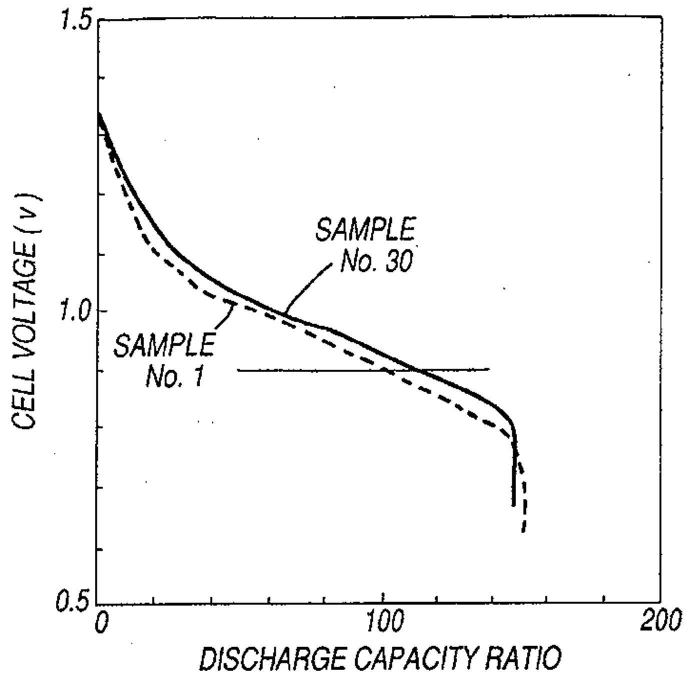
1.5
1.0
0.5
CELL VOLTAGE (v)
SAMPLE
No. 30
SAMPLE
No. 1
0
100
200
DISCHARGE CAPACITY RATIO

Fig. 5

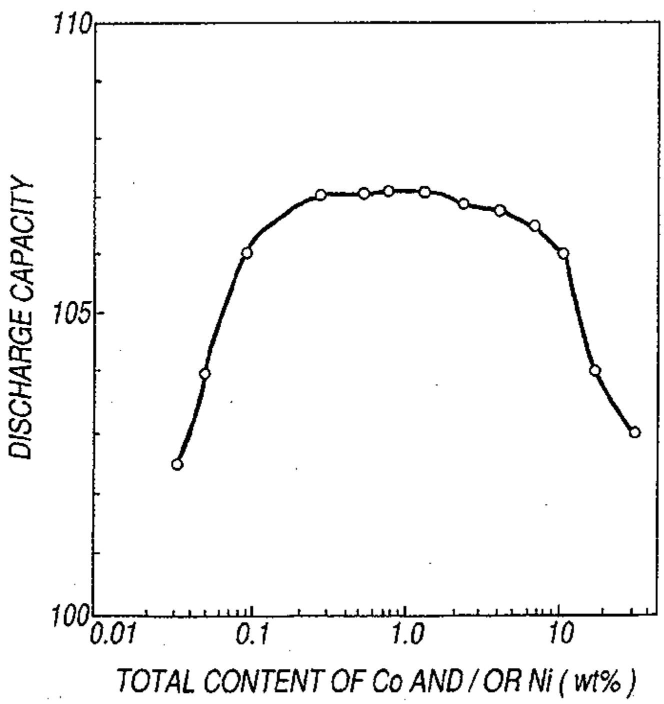
110
105
100
DISCHARGE CAPACITY
0.01
0.1
1.0
10
TOTAL CONTENT OF Co AND / OR Ni (wt%)

Fig. 6

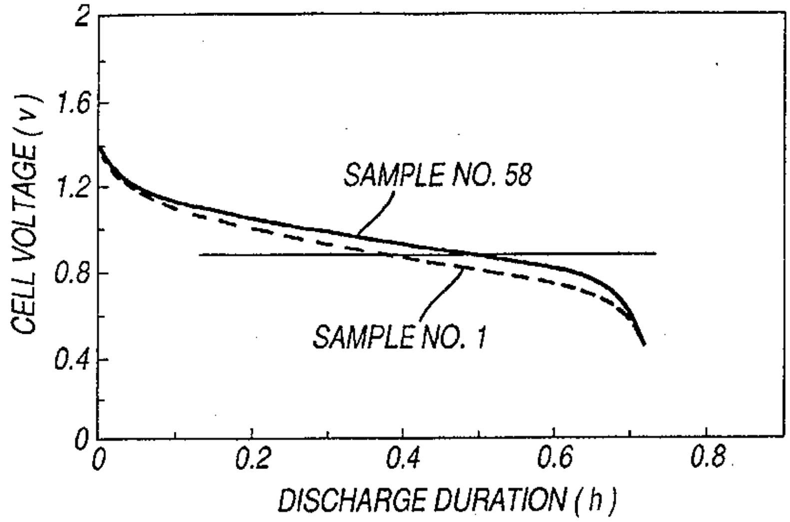
2
1.6
1.2
0.8
0.4
0
CELL VOLTAGE (v)
SAMPLE NO. 58
SAMPLE NO. 1
0
0.2
0.4
0.6
0.8
DISCHARGE DURATION (h)

Fig. 7

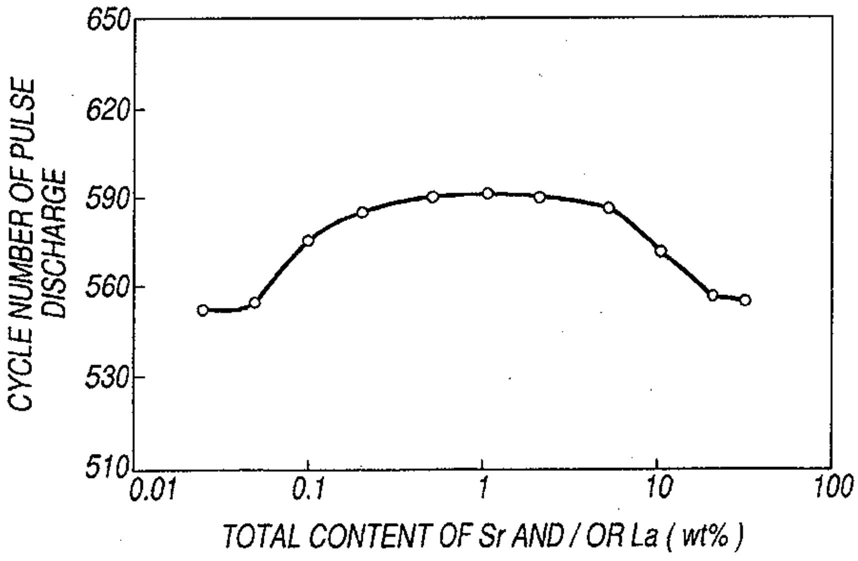
650
620
590
560
530
510
CYCLE NUMBER OF PULSE DISCHARGE
0.01
0.1
1
10
100
TOTAL CONTENT OF Sr AND / OR La (wt%)

Fig. 8

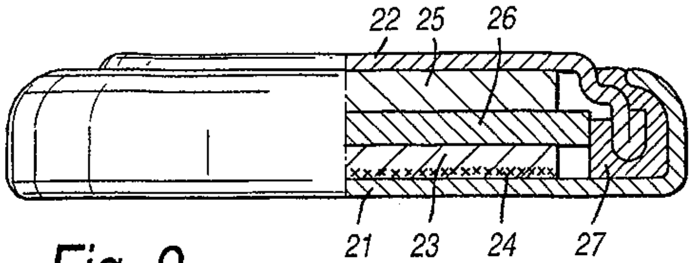

Fig. 9

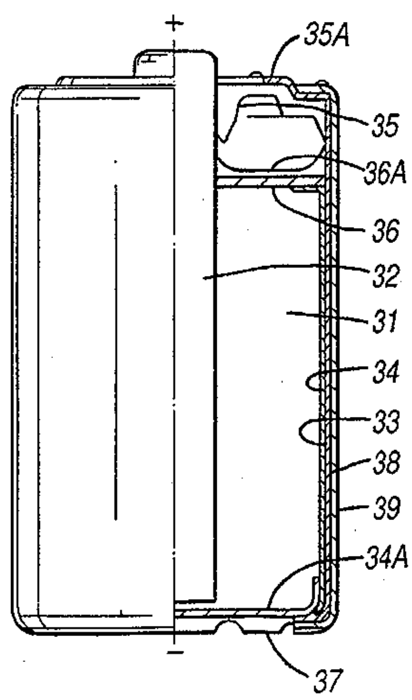

Fig. 10

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 30 0663

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	PATENT ABSTRACTS OF JAPAN vol. 011, no. 083 (E-489), 13 March 1987 & JP 61 237366 A (MATSUSHITA ELECTRIC IND CO LTD), 22 October 1986, * abstract * ---	1	H01M4/50 C01G45/02
D,A	US 5 342 712 A (MIECZKOWSKA JOLA E ET AL) 30 August 1994 * claim 1 * ---	1	
A	WO 93 18557 A (BATTERY TECHNOLOGIES INC) 16 September 1993 * claims 7,8 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			H01M C01G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29 May 1997	Andrews, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)